WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(21) International Application Number: PCT/US99/25155 (22) International Filing Date: 27 October 1999 (27.10.99) (23) Priority Data: 27 October 1999 (27.10.99) (24) Priority Data: 28 November 1998 (12.11.98) US (99/19),002 12 November 1998 (12.11.98) US (99/19),003 12 November 1998 (12.11.98) US (99/19),003 12 November 1998 (12.11.98) US (71) Applicant: COLGATE-PALMOLIVE COMPANY [US/US]; 300 Park Avenue, New York, NY 10022 (US). (72) Inventor: MERTENS, Baudouin; Avenue de la Dame 34, B-5100 Jambes (BE). (74) Agent: NANFELDT, Richard, E.; Colgate-Palmolive Company, 909 River Road, P.O. Box 1343, Piscataway, NJ 08855-1343 (US).	(51) International Patent Classification 7 : C11D 1/00	A2	(11) International Publication Number: WO 00/29528 (43) International Publication Date: 25 May 2000 (25.05.00)
	(22) International Filing Date: 27 October 1999 (2) (30) Priority Data: 09/191,002 12 November 1998 (12.11.9 09/191,003 12 November 1998 (12.11.9 (71) Applicant: COLGATE-PALMOLIVB COMPANY 300 Park Avenue, New York, NY 10022 (US). (72) Inventor: MERTENS, Baudouin; Avenue de la E B-5100 Jambes (BE). (74) Agent: NANFELDT, Richard, E.; Colgate-Palmolipany, 909 River Road, P.O. Box 1343, Piscatu	27.10.9 8) U 8) U [US/U: Dame 3	BR. BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, P, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, FP, RO, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARTIPO patent (GI, GM, KE, LS, MW, SD, SI, SZ, TZ, UG, ZW), Burasian patent (AM, AZ, BY, KG, KZ, MD, RU, TI, TM), Europea patent (AT, BE, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published Without international search report and to be republished upon receipt of that report.

(57) Abstract

An improvement is described in all purpose liquid cleaning composition and microemulsion composition which are especially effective in the removal of oily and greasy soil and contains an anionic detergent, a nonionic surfactant, a short chain amphiphile, a hydrocarbon ingredient, and water.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

	AL	Albania	ES	Spain	LS	Lesotho	St	Slovenia
Autoralia	AM	Armenia	FI	Finland	LT	Lithuania	sk	Slovakia
Azerbaljan	AT.	Austria	FR	France	LU	Luxembourg	SN	Senegal
Banil	ΑU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
Barbudos	AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
Belgium	BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
Barkina Piaco Greece Republic of Mendonia TR Trukey	BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
	BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
	BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
Brazil L	BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
Belima	BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
Canada	BR	Brazil	IL,	Israel	MR	Mauritania	υG	Uganda
CP Central African Republic JP Jepan NE Niger VN Vist Nam CU Cong Cong KE Kersys NL Netherhands VU Yupostavis CH Switzerland KG Kyrgystsan NO Norway ZW Zimbabwe CL Chef Velovie KP Democracil People's NZ New Zealand Velovie Velovie		Belarus	LS	Iceland	MW	Malawi	US	United States of America
Congo KE Keryx NL Notherlands YU Yugoslavia		Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CH Switzerland KG Kyrgystan NO Norway ZW Zimbabwe CL Cted fVolve KP Democracil People's NZ New Zealand CM China KR Republic of Korea PL Poland CV China KR Republic of Korea PT Potrupal CU Cuba KZ Katakatuna RO Romania CZ Czech Republic LC Saint Lucia-i RU Rassim Feberation DE Germany L1 Liechtenstein SD Sudan DK Demnark LK Sri Lanka SE Sweden	CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
C1 C26 d'Hofre KP Democraile People's NZ New Zealand				Kenya	NL	Netherlands	YU	Yugoslavia
CM Camertron Republic of Kores P.L Poland CN China K.R Republic of Kores P.T Portugal CU Cuba K.Z Katakatune RO Romania CZ Czech Republic L.C Saint Bacia RU Rassinne Rederation DE Germany L.I Liechtenstein SD Sudan DK Denmark L.K Sri Lanka SE Sweden	CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CN Cinita KR Republic of Korea PT Portugal CU Cuba KZ Kazakstras RO Romania CZ Czech Republic LC Saint Lacia RU Russium Pederation DE Germany L1 Lichinensiein SD Sudan DK Denmark LK Sri Lanka SE Sweden		Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CU Cuba KZ Katakatun RO Romania CZ Czech Republic LC Saint Lucia RU Rasainn Bederaflon DE Germany LI Liechtenstein SD Sudan DK Demmark LI Ki Lanka SE Sweden	CM	Cameroon		Republic of Korea	PL	Poland		
CZ Czech Republic LC Saint Lucia RU Rusarian Pederation DE Germany LI Lichitentelin SD Sodan DK Denmark LK ST Lanka SE Sweden		China	KR	Republic of Korea	PT	Portugal		
DE Germany LI Liechtenstein SD Sudan DK Denmark LK Sri Lanka SE Sweden		Cuba	KZ	Kazakstan	RO	Romania		
DK Denmark LK Sri Lanka SE Sweden		Czech Republic	LC	Saint Lucia	RU	Russian Pederation		
		Germany		Liechtenstein	SD	Sudan		
		Denmark	LK	Sri Lanka	SE	Sweden		
KE Estonia LK Liberia SG Singapore	EE	Estonia	1.R	Liberia	SG	Singspore		

WO 00/29528 PCT/US99/25155

MICROEMULSION LIQUID CLEANING COMPOSITION CONTAINING A SHORT CHAIN AMPHIPHILE

Field of the Invention

5

10

15

20

25

The present invention relates to liquid cleaning microemulsion composition containing short chain amphiphiles.

Background of the Invention

This invention relates to an improved all-purpose liquid cleaning composition or a microemulsion composition having excellent foam collapse properties and excellent grease cutting properties designed in particular for cleaning hard surfaces and which is effective in removing grease soil and/or bath soil and in leaving unrinsed surfaces with a shiny appearance.

In recent years all-purpose liquid detergents have become widely accepted for cleaning hard surfaces, e.g., painted woodwork and panels, tiled walls, wash bowls, bathtubs, linoleum or tile floors, washable wall paper, etc. Such all-purpose liquids comprise clear and opaque aqueous mixtures of water-soluble synthetic organic detergents and water-soluble detergent builder salts. In order to achieve comparable cleaning efficiency with granular or powdered all-purpose cleaning compositions, use of water-soluble inorganic phosphate builder salts was favored in the prior art all-purpose liquids. For example, such early phosphate-containing compositions are described in U.S. Patent Nos. 2.560.839; 3.234.138; 3.350.319; and British Patent No. 1.223.739.

In view of the environmentalist's efforts to reduce phosphate levels in ground water, improved all-purpose liquids containing reduced concentrations of inorganic phosphate builder salts or non-phosphate builder salts have appeared. A particularly useful self-opacified liquid of the latter type is described in U.S. Patent No. 4,244,840.

However, these prior art all-purpose liquid detergents containing detergent builder salts or other equivalent tend to leave films, spots or streaks on cleaned unrinsed surfaces, particularly shiny surfaces. Thus, such liquids require thorough rinsing of the cleaned surfaces which is a time-consuming chore for the user. In order to overcome the foregoing disadvantage of the prior art all-purpose liquid, U.S. Patent No. 4,017,409 teaches that a mixture of paraffin sulfonate and a reduced concentration of inorganic phosphate builder salt should be employed. However, such compositions are not completely acceptable from an environmental point of view based upon the phosphate content. On the other hand, another alternative to achieving phosphate-free all-purpose liquids has been to use a major proportion of a mixture of anionic and nonionic detergents with minor amounts of glycol ether solvent and organic amine as shown in U.S. Patent No. 3,935,130. Again, this approach has not been completely satisfactory and the high levels of organic detergents necessary to achieve cleaning cause foaming which, in turn, leads to the need for thorough rinsing which has been found to be undesirable to today's consumers.

5

10

15

20

25

Another approach to formulating hard surfaced or all-purpose liquid detergent composition where product homogeneity and clarity are important considerations involves the formation of oil-in-water (o/w) microemulsions which contain one or more surface-active detergent compounds, a water-immiscible solvent (typically a hydrocarbon solvent), water and a "cosurfactant" compound which provides product stability. By definition, an o/w microemulsion is a spontaneously forming colloidal dispersion of "oil" phase particles having a particle size in the range of 25 to 800 Å in a continuous aqueous phase.

In view of the extremely fine particle size of the dispersed oil phase particles, microemulsions are transparent to light and are clear and usually highly stable against phase separation.

Patent disclosures relating to use of grease-removal solvents in o/w microemulsions include, for example, European Patent Applications EP 0137615 and EP 0137616 - Herbots et al; European Patent Application EP 0160762 - Johnston et al; and U.S. Patent No. 4,561,991 - Herbots et al. Each of these patent disclosures also teaches using at least 5% by weight of grease-removal solvent.

It also is known from British Patent Application GB 2144763A to Herbots et al, published March 13, 1985, that magnesium salts enhance grease-removal performance of organic grease-removal solvents, such as the terpenes, in o/w microemulsion liquid detergent compositions. The compositions of this invention described by Herbots et al. require at least 5% of the mixture of grease-removal solvent and magnesium salt and preferably at least 5% of solvent (which may be a mixture of water-immiscible non-polar solvent with a sparingly soluble slightly polar solvent) and at least 0.1% magnesium salt.

5

10

15

20

25

However, since the amount of water immiscible and sparingly soluble components which can be present in an o/w microemulsion, with low total active ingredients without impairing the stability of the microemulsion is rather limited (for example, up to 18% by weight of the aqueous phase), the presence of such high quantities of grease-removal solvent tend to reduce the total amount of greasy or oily soils which can be taken up by and into the microemulsion without causing phase separation.

The following representative prior art patents also relate to liquid detergent cleaning compositions in the form of o/w microemulsions: U.S. Patents No. 4,472,291 - Rosario; U.S. Patent No. 4,540,448 - Gauteer et al; U.S. Patent No. 3,723,330 - Sheffin; etc.

Liquid detergent compositions which include terpenes, such as d-limonene, or other grease-removal solvent, although not disclosed to be in the form of o/w microemulsions, are the subject matter of the following representative patent documents: European Patent Application 0080749; British Patent Specification 1,603,047; and U.S. Patent Nos. 4,414,128 and 4,540,505. For example, U.S. Patent No. 4,414,128 broadly discloses an aqueous liquid detergent composition characterized by, by weight:

 (a) from 1% to 20% of a synthetic anionic, nonionic, amphoteric or zwitterionic surfactant or mixture thereof:

- (b) from 0.5% to 10% of a mono- or sesquiterpene or mixture thereof, at a weight ratio of (a):(b) being in the range of 5:1 to 1:3; and
- (c) from 0.5% 10% of a polar solvent having a solubility in water at 15°C in the range of from 0.2% to 10%. Other ingredients present in the formulations disclosed in this patent include from 0.05% to 2% by weight of an alkali metal, ammonium or alkanolammonium soap of a C13-C24 fatty acid; a calcium sequestrant from 0.5% to 13% by weight; non-aqueous solvent, e.g., alcohols and glycol ethers, up to 10% by weight; and hydrotropes, e.g., urea, ethanolamines, salts of lower alkylaryl sulfonates, up to 10% by weight. All of the formulations shown in the Examples of this patent include relatively large amounts of detergent builder salts which are detrimental to surface shine.

Summary of the Invention

10

15

20

25

The present invention provides an improved, liquid cleaning composition having excellent foam collapse properties and excellent grease cutting property in the form of a microemulsion which is suitable for cleaning hard surfaces such as plastic, vitreous and metal surfaces having a shiny finish, oil stained floors, automotive engines and other engines. More particularly, the improved cleaning compositions, with excellent foam collapse properties and excellent grease cutting property exhibit good grease soil removal properties due to the improved interfacial tensions, when used in undiluted (neat) or dilute form and leave the cleaned surfaces shiny without the need of or requiring only minimal additional rinsing or wiping. The latter characteristic is evidenced by little or no visible residues on the unrinsed cleaned surfaces and, accordingly, overcomes one of the disadvantages of prior art products.

Surprisingly, these desirable results are accomplished even in the absence of polyphosphate or other inorganic or organic detergent builder salts and also in the complete absence or substantially complete absence of grease-removal solvent.

In one aspect, the invention generally provides a stable, optically clear microemulsion, hard surface cleaning composition especially effective in the removal of oily and greasy oil, which is in the form of a substantially dilute oil-in-water

microemulsion having an aqueous phase and an oil phase; The dilute microemulsion composition includes, on a weight basis:

0.1% to 8% of a sulfonate anionic surfactant:

0.5% to 6% of an ethoxylated polyhydric alcohol type compound (as defined below) an ethoxylated/propoxylated nonionic surfactant and an ethoxylated nonionic surfactant and mixtures thereof:

0.5% to 8% of a short chain amphiphile;

0.25% to 6% of magnesium sulfate heptahydrate:

0.05% to 2% of a fatty acid:

5

10

15

20

25

0.1% to 50% of a perfume, essential oil, or water insoluble hydrocarbon having 6 to 18 carbon atoms; and

the balance being water, wherein the composition does not contain a water-soluble polyethylene glycols having a molecular weight of 150 to 1000, polypropylene glycol of the formula HO(CH₃CHCH₂O)_nH wherein n is a number from 2 to 18, mixtures of polyethylene glycol and polypropylene glycol (Synalox) and mono and di C₁-C₆ alkyl ethers and esters of ethylene glycol and propylene glycol having the structural formulas R(X)_nOH, R₁(X)_nOH, R(X)_nOR and R₁(X)_nOR₁wherein R is C₁-C₆ alkyl group, R₁ is C₂-C₄ acyl group, X is (OCH₂CH₂) or (OCH₂(CH₃)CH) and n is a number from 1 to 4, diethylene glycol, triethylene glycol, an alkyl lactate, wherein the alkyl group has 1 to 6 carbon atoms, 1methoxy-2-propanol, 1methoxy-3-propanol, and 1methoxy 2-, 3- or 4-butanol.

Excluded from the instant microemulsion and all purpose cleaning compositions are grease release agents characterized by the formula:

wherein R₁ is a methyl group and R₂, R₃ and R₄ are independently selected from the group consisting of methyl, ethyl, and CH₂CH₂Y, wherein Y is selected from the group

consisting of CI, Br, CO₂H, (CH₂O)_nOH wherein n=1 to 10, OH, CH₂CH₉OH and x is selected from the group consisting of CI, Br, methosulfate

and _HCO3

5

10

15

20

25

Also excluded from the instant microemulsion or all purpose cleaning compositions are grease release agents which are an ethoxylated maleic anhydride-alpha-olefin copolymer having a comblike structure with both hydrophobic and hydrophilic chains and is depicted by the formula:

wherein n is 5 to 14, preferably 7 to 9, x is 7 to 19, preferably 8 to 19 and y is of such a value as to provide a molecular weight 10,000 to 30,000.

У

Detailed Description of the Invention

The present invention relates to a stable optically clear microemulsion composition comprising by weight: 0.1% to 8% of a sulfonate anionic surfactant, 0.05% to 2% of a fatty acid; 0.5% to 8% of a short chain amphiphile; 0.25% to 6% of magnesium sulfate heptahydrate; 0.5% to 6% of a nonionic surfactant selected from the group consisting of ethoxylated nonionics, surfactants, ethoxylated/propylated nonionic surfactant; and ethoxylated polyhydric alcohol type compound and mixtures thereof; 0.1% to 6% of a water insoluble hydrocarbon, essential oil or a perfume, 0.05% to 2% of a fatty acid and the balance being water.

According to the present invention, the role of the water insoluble hydrocarbon can be provided by a non-water-soluble perfume. Typically, in aqueous based compositions the presence of a solubilizers, such as alkali metal lower alkyl aryl

sulfonate hydrotrope, triethanolamine, urea, etc., is required for perfume dissolution, especially at perfume levels of 1% and higher, since perfumes are generally a mixture of fragrant essential oils and aromatic compounds which are generally not water-soluble. Therefore, by incorporating the perfume into the aqueous cleaning composition as the oil (hydrocarbon) phase of the ultimate o/w microemulsion composition, several different important advantages are achieved.

5

10

15

20

25

As used herein and in the appended claims the term "perfume" is used in its ordinary sense to refer to and include any non-water soluble fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flower, herb, blossom or plant), artificial (i.e., mixture of natural oils or oil constituents) and synthetically produced substance) odoriferous substances. Typically, perfumes are complex mixtures of blends of various organic compounds such as alcohols, aldehydes, ethers, aromatic compounds and varying amounts of essential oils (e.g., terpenes) such as from 0% to 80%, usually from 10% to 70% by weight, the essential oils themselves being volatile odoriferous compounds and also serving to dissolve the other components of the perfume.

In the present invention the precise composition of the perfume is of no particular consequence to cleaning performance so long as it meets the criteria of water immiscibility and having a pleasing odor. Naturally, of course, especially for cleaning compositions intended for use in the home, the perfume, as well as all other ingredients, should be cosmetically acceptable, i.e., non-toxic, hypoallergenic, etc.. The instant compositions show a marked improvement in ecotoxocity as compared to existing commercial products.

The hydrocarbon such as a perfume is present in the dilute o/w microemulsion in an amount of from 0.1% to 6% by weight, preferably from 0.4% to 5% by weight. If the amount of hydrocarbon (perfume) is less than 0.4% by weight it becomes difficult to form the o/w microemulsion. If the hydrocarbon (perfume) is added in amounts more than 10% by weight, the cost is increased without any additional cleaning benefit and, in fact, with some diminishing of cleaning performance insofar as the total amount of

greasy or oily soil which can be taken up in the oil phase of the microemulsion will decrease proportionately. In the all purpose hard surface cleaning composition which is not a microemulsion the concentration of the perfume is 0 to 10 wt. %, more preferably 0.1 wt. % to 10 wt. %

In place of the perfume in either the microemulsion composition or the all purpose hard surface cleaning composition at the same previously defined concentrations that the perfume was used in either the microemulsion or the all purpose hard surface cleaning composition one can employ an essential oil or a water insoluble hydrocarbon having 6 to 18 carbon such as a paraffin or isoparaffin.

5

10

15

20

25

Suitable essential oils are selected from the group consisting of: Anethole 20/21 natural, Aniseed oil china star, Aniseed oil globe brand, Balsam (Peru), Basil oil (India), Black pepper oil, Black pepper oleoresin 40/20, Bois de Rose (Brazil) FOB, Borneol Flakes (China), Camphor oil, White, Camphor powder synthetic technical, Cananga oil (Java), Cardamom oil, Cassia oil (China), Cedarwood oil (China) BP, Cinnamon bark oil, Cinnamon leaf oil, Citronella oil, Clove bud oil, Clove leaf, Coriander (Russia), Coumarin 69°C (China), Cyclamen Aldehyde, Diphenyl oxide, Ethyl vanilin, Eucalyptol, Eucalyptus oil, Eucalyptus citriodora, Fennel oil, Geranium oil, Ginger oil, Ginger oleoresin (India), White grapefruit oil, Guaiacwood oil, Gurjun balsam, Heliotropin, Isobornyl acetate, Isolongifolene, Juniper berry oil, L-methyl acetate, Lavender oil, Lemon oil, Lemongrass oil, Lime oil distilled, Litsea Cubeba oil, Longifolene, Menthol crystals, Methyl cedryl ketone, Methyl chavicol, Methyl salicylate. Musk ambrette, Musk ketone, Musk xylol, Nutmeg oil, Orange oil, Patchouli oil, Peppermint oil, Phenyl ethyl alcohol, Pimento berry oil, Pimento leaf oil, Rosalin, Sandalwood oil, Sandenol, Sage oil, Clary sage, Sassafras oil, Spearmint oil, Spike lavender, Tagetes, Tea tree oil, Vanilin, Vetyver oil (Java), Wintergreen

Suitable water-soluble non-soap, anionic surfactants include those surfaceactive or detergent compounds which contain an organic hydrophobic group containing generally 8 to 26 carbon atoms and preferably 10 to 18 carbon atoms in their molecular structure and at least one water-solubilizing group which is sulfonate group, so as to form a water-soluble detergent. Usually, the hydrophobic group will include or comprise a Ce-C22 alkyl, alkyl or acyl group. Such surfactants are employed in the form of water-soluble salts and the salt-forming cation usually is selected from the group consisting of sodium, potassium, ammonium, magnesium and mono-, di- or tri-C2-C3 alkanolammonium, with the sodium, magnesium and ammonium cations again being preferred.

Examples of suitable sulfonated anionic surfactants are the well known higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, C8-C15 alkyl toluene sulfonates and C8-C15 alkyl phenol sulfonates.

10

15

20

25

One preferred sulfonate surfactant is a linear alkyl benzene sulfonate having a high content of 3- (or higher) phenyl isomers and a correspondingly low content (well below 50%) of 2- (or lower) phenyl isomers, that is, wherein the benzene ring is preferably attached in large part at the 3 or higher (for example, 4, 5, 6 or 7) position of the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1 position is correspondingly low. Particularly preferred materials are set forth in U.S. Patent 3.320.174.

Other suitable anionic surfactants are the olefin sulfonates, including long-chain alkene sulfonates, long-chain hydroxyalkane sulfonates or mixtures of alkene sulfonates and hydroxyalkane sulfonates. These olefin sulfonate detergents may be prepared in a known manner by the reaction of sulfur trioxide (SO3) with long-chain olefins containing 8 to 25, preferably 12 to 21 carbon atoms and having the formula RCH=CHR1 where R is a higher alkyl group of 6 to 23 carbons and R1 is an alkyl group of 1 to 17 carbons or hydrogen to form a mixture of sultones and alkene sulfonic acids which is then treated to convert the sultones to sulfonates. Preferred olefin sulfonates contain from 14 to 16 carbon atoms in the R alkyl group and are obtained by sulfonating an a-olefin.

Other example of operative anionic surfactants includes sodium dioctyl sulfosuccinate [di-(2 ethylhexyl) sodium sulfosuccinate being one] and corresponding dihexyl and dioctyl esters. The preferred sulfosuccinic acid ester salts are esters of aliphitic alcohols such as saturated alkanols of 4 to 12 carbon atoms and are normally diesters of such alkanols. More preferably such are alkali metal salts of the diesters of alcohols of 6 to 10 carbons atoms and more preferably the diesters will be from octanol, such as 2 -ethyl hexanol, and the sulfonic acid salt will be the sodium salt.

5

10

15

20

25

Especially preferred anionic sulfonate surfactants are paraffin sulfonates containing 10 to 20, preferably 13 to 17, carbon atoms. Primary paraffin sulfonates are made by reacting long-chain alpha olefins and bisulfites and paraffin sulfonates having the sulfonate group distributed along the paraffin chain are shown in U.S. Patents Nos. 2,503,280; 2,507,088; 3,260,744; 3,372,188; and German Patent 735,096.

Of the foregoing non-soap anionic sulfonate surfactants, the preferred surfactants are the magnesium salt of the C13-C17 paraffin or alkane sulfonates.

Generally, the proportion of the nonsoap-anionic surfactant will be in the range of 0.1% to 8%, preferably from 1% to 6%, by weight of the dilute microemulsion composition.

The instant composition contains 0.5 wt. % to 6 wt. %, more preferably 1.0 wt. % to 5 wt. % of a nonionic surfactant selected from the group of an aliphatic ethoxylated nonionic surfactant, an ethoxylated polyhydric alcohol and an aliphatic ethoxylated/propoxylated nonionic surfactant.

The water soluble aliphatic ethoxylated nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates and secondary aliphatic alcohol ethoxylates. The length of the polyethenoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

The nonionic surfactant class includes the condensation products of a higher alcohol (e.g., an alkanol containing 8 to 16 carbon atoms in a straight or branched chain configuration) condensed with 4 to 20 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with 16 moles of ethylene oxide (EO), tridecanol condensed with 6 to 15 moles of EO, myristyl alcohol condensed with 10 moles of EO

per mole of myristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms in length and wherein the condensate contains either 6 moles of EO per mole of total alcohol or 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing 9-15 carbon atoms, such as C9-C11 alkanol condensed with 4 to 10 moles of ethylene oxide (Neodol 91-8 or Neodol 91-5), C12-13 alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C12-15 alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C14-15 alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrophobic lipophilic balance) value of 8 to 15 and give good O/W emulsification, whereas ethoxamers with HLB values below 7 contain less than 4 ethyleneoxide groups and tend to be poor emulsifiers and poor detergents.

10

15

20

25

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of the foregoing type are C11-C15 secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

The ethoxylated polyhydric alcohol type compound such as an ethoxylated glycerol type compound) is a mixture of a fully esterified ethoxylated polyhydric alcohol, a partially esterified ethoxylated polyhydric alcohol and a nonesterified ethoxylated polyhydric alcohol, wherein the preferred polyhydric alcohol is glycerol, and the compound is

and

5

10

15

20

wherein w equals one to four, most preferably one, and B is selected from the group consisting of hydrogen or a group represented by:

wherein R is selected from the group consisting of alkyl group having 6 to 22 carbon atoms, more preferably 11 to 15 carbon atoms and alkenyl groups having 6 to 22 carbon atoms, more preferably 11 to 15 carbon atoms, wherein a hydrogenated tallow alkyl chain or a coco alkyl chain is most preferred, wherein at least one of the B groups is represented by said

25 and R¹ is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, more preferably 0 to 40, provided that (x+y+z) equals 2 to 100, preferably 4 to 24 and most preferably 4 to 19, wherein in Formula (I) the weight ratio of monoester / diester / triester is 40 to 90 / 5 to 35 / 1 to 20, more preferably 50 to 90 / 9 to 32 / 1 to 12, wherein the weight ratio of Formula (I) to Formula

(II) is a value between 3 to 0.02, preferably 3 to 0.1, most preferably 1.5 to 0.2, wherein it is most preferred that there is more of Formula (II) than Formula (I) in the mixture that forms the compound.

The ethoxylated glycerol type compound used in the instant composition is manufactured by the Kao Corporation and sold under the trade name Levenol such as Levenol F-200 which has an average EO of 6 and a molar ratio of coco fatty acid to glycerol of 0.55 or Levenol V501/2 which has an average EO of 17 and a molar ratio of tallow fatty acid to glycerol of 1.0. It is preferred that the molar ratio of the fatty acid to glycerol is less than 1.7, more preferably less than 1.5 and most preferably less than 1.0. The ethoxylated glycerol type compound has a molecular weight of 400 to 1600, and a pH (50 grams / liter of water) of 5-7. The Levenol compounds are substantially non irritant to human skin and have a primary biodegradabillity higher than 90% as measured by the Wickbold method Bias-7d.

5

10

15

20

25

Two examples of the Levenol compounds are Levenol V-501/2 which has 17 ethoxylated groups and is derived from tallow fatty acid with a fatty acid to glycerol ratio of 1.0 and a molecular weight of 1465 and Levenol F-200 has 6 ethoxylated groups and is derived from coco fatty acid with a fatty acid to glycerol ratio of 0.55. Both Levenol F-200 and Levenol V-501/2 are composed of a mixture of Formula (I) and Formula (II). The Levenol compounds has ecoxicity values of algae growth inhibition > 100 mg/liter; acute toxicity for Daphniae > 100 mg/liter and acute fish toxicity > 100 mg/liter. The Levenol compounds have a ready biodegradability higher than 60% which is the minimum required value according to OECD 301B measurement to be acceptably biodegradable.

Polyesterified nonionic compounds also useful in the instant compositions are Crovol PK-40 and Crovol PK-70 manufactured by Croda GMBH of the Netherlands. Crovol PK-40 is a polyoxyethylene (12) Palm Kernel Glyceride which has 12 EO groups. Crovol PK-70 which is preferred is a polyoxyethylene (45) Palm Kernel Glyceride have 45 EO groups.

The water soluble nonionic surfactants which can be utilized in this invention are an aliphatic ethoxylated/propoxylated nonionic surfactants which are depicted by the formula:

5 c

10

wherein R is a branched chain alkyl group having 10 to 16 carbon atoms, preferably an isotridecyl group and x and y are independently numbered from 1 to 20. A preferred ethoxylated/propoxylated nonionic surfactant is Plurafac* 300 manufactured by BASF.

The composition contains 0.5 wt. % to 8 wt. %, more preferably 1 wt. % to 6 wt. % of a short chain amphiphile which is not a surfactant and is characterized by the formula:

or

or

20

25

wherein R₁ or R₂ or R₃ are a straight or branched chain alkyl group having 2 to 6 carbon atoms and x or w is a number from 2 to 5, more preferably 2 to 4 and n is a number from 2 to 8, more preferably 3 to 6 and y or z is a number from 1 to 4, more preferably 1 to 3 and the amphiphile has an HLB of 6 to 9, preferably 7 to 8. Preferred amphiphiles have a C₆ alkyl group and 2 to 5 EO such as hexanol 5EO.

The composition also contains an inorganic or organic salt of oxide of a multivalent metal cation, particularly Mg++. The metal salt or oxide provides several benefits including improved cleaning performance in dilute usage, particularly in soft water areas, and minimized amounts of perfume required to obtain the microemulsion

state. Magnesium sulfate, either anhydrous or hydrated (e.g., heptahydrate), is especially preferred as the magnesium salt. Good results also have been obtained with magnesium oxide, magnesium chloride, magnesium acetate, magnesium propionate and magnesium hydroxide. These magnesium salts can be used with formulations at neutral or acidic pH since magnesium hydroxide will not precipitate at these pH levels.

5

10

15

20

25

Although magnesium is the preferred multivalent metal from which the salts (inclusive of the oxide and hydroxide) are formed, other polyvalent metal ions also can be used provided that their salts are nontoxic and are soluble in the aqueous phase of the system at the desired pH level,

Thus, depending on such factors as the pH of the system, the nature of the primary surfactants and amphiphiles, and so on, as well as the availability and cost factors, other suitable polyvalent metal ions include aluminum, copper, nickel, iron, calcium, etc. It should be noted, for example, that with the preferred paraffin sulfonate anionic detergent calcium salts will precipitate and should not be used. It has also been found that the aluminum salts work best at pH below 5 or when a low level, for example 1 weight percent, of citric acid is added to the composition which is designed to have a neutral pH. Alternatively, the aluminum salt can be directly added as the citrate in such case. As the salt, the same general classes of anions as mentioned for the magnesium salts can be used, such as halide (e.g., bromide, chloride), sulfate, nitrate, hydroxide, oxide, acetate, propionate, etc.

Preferably, in the dilute compositions the metal compound is added to the composition in an amount sufficient to provide at least a stoichiometric equivalent between the anionic surfactant and the multivalent metal cation. For example, for each gram-ion of Mg++ there will be 2 gram moles of paraffin sulfonate, alkylbenzene sulfonate, etc., while for each gram-ion of Al³⁺ there will be 3 gram moles of anionic surfactant. Thus, the proportion of the multivalent salt generally will be selected so that one equivalent of compound will neutralize from 0.1 to 1.5 equivalents, preferably 0.9 to 1.4 equivalents, of the acid form of the anionic surfactant. At higher concentrations of

anionic surfactant, the amount of multivalent salt will be in range of 0.5 to 1 equivalents per equivalent of anionic surfactant.

The microemulsion compositions can include from 0.05% to 2.0% by weight of the composition of a Cg-C₂₂ fatty acid or fatty acid soap as a foam suppressant.

5

10

15

20

25

The addition of fatty acid or fatty acid soap provides an improvement in the rinseability of the composition whether applied in neat or diluted form. Generally, however, it is necessary to increase the level of cosurfactant to maintain product stability when the fatty acid or soap is present. If more than 2.5 wt. % of a fatty acid is used in the instant compositions, the composition will become unstable at low temperatures as well as having an objectionable smell.

As example of the fatty acids which can be used as such or in the form of soap, mention can be made of distilled coconut oil fatty acids, "mixed vegetable" type fatty acids (e.g. high percent of saturated, mono-and/or polyunsaturated C₁₈ chains); oleic acid, stearic acid, palmitic acid, eiocosanoic acid, and the like, generally those fatty acids having from 8 to 22 carbon atoms being acceptable.

The final essential ingredient in the inventive microemulsion compositions or all purpose hard surface cleaning compositions having improved interfacial tension properties is water. The proportion of water in the microemulsion or all purpose hard surface cleaning composition compositions generally is in the range of 20% to 97%, preferably 70% to 97% by weight.

The liquid cleaning composition of this invention may, if desired, also contain other components either to provide additional effect or to make the product more attractive to the consumer. The following are mentioned by way of example: Colors or dyes in amounts up to 0.5% by weight; bactericides in amounts up to 1% by weight; preservatives or antioxidizing agents, such as formalin, 5-bromo-5-nitro-dioxan-1,3; 5-chloro-2-methyl-4-isothaliazolin-3-one, 2,6-di-tert.butyl-p-cresol, etc., in amounts up to 2% by weight; and pH adjusting agents, such as sulfuric acid or sodium hydroxide, as needed. Furthermore, if opaque compositions are desired, up to 4% by weight of an opacifier may be added.

In final form, the microemulsions exhibit stability at reduced and increased temperatures. More specifically, such compositions remain clear and stable in the range of 4°C to 50°C, especially 2°C to 43°C. Such compositions exhibit a pH in the acid or neutral range depending on intended end use. The liquids are readily pourable and exhibit a viscosity in the range of 6 to 60 milliPascal second (mPas.) as measured at 25°C with a Brookfield RVT Viscometer using a #1 spindle rotating at 20 RPM. Preferably, the viscosity is maintained in the range of 10 to 40 mPas.

5

10

15

20

25

The compositions are directly ready for use or can be diluted as desired and in either case no or only minimal rinsing is required and substantially no residue or streaks are left behind. Furthermore, because the compositions are free of detergent builders such as alkali metal polyphosphates they are environmentally acceptable and provide a better "shine" on cleaned hard surfaces.

When intended for use in the neat form, the liquid compositions can be packaged under pressure in an aerosol container or in a pump-type sprayer for the so-called spray-and-wipe type of application.

Because the compositions as prepared are aqueous liquid formulations and since no particular mixing is required to form the microemulsion, the compositions are easily prepared simply by combining all the ingredients in a suitable vessel or container. The order of mixing the ingredients is not particularly important and generally the various ingredients can be added sequentially or all at once or in the form of aqueous solutions of each or all of the surfactants and amphiphiles can be separately prepared and combined with each other and with the perfume. The magnesium salt, or other multivalent metal compound, when present, can be added as an aqueous solution thereof or can be added directly. It is not necessary to use elevated temperatures in the formation step and room temperature is sufficient.

The instant microemulsion formulas explicitly exclude alkali metal silicates and alkali metal builders such as alkali metal polyphosphates, alkali metal carbonates, alkali metal phosphonates and alkali metal citrates because these materials, if used in the

instant composition, would cause the composition to have a high pH as well as leaving

residue on the surface being cleaned.

5

10

The following examples illustrate liquid cleaning compositions of the described invention. Unless otherwise specified, all percentages are by weight. The exemplified compositions are illustrative only and do not limit the scope of the invention. Unless otherwise specified, the proportions in the examples and elsewhere in the specification are by weight.

Example 1

The following compositions in wt. % were prepared by simple mixing at 25°C:

	D=4	_	
	Ref.	Α	В
Sodium C ₁₃ -C ₁₇ paraffin sulfonate	3.36	2	2
Levenoi F-200	0.9		2
LF300	0.9		
Dobanol 91-5		2	
Diethylene glycol monobutyl ether	4.8		
Hexanol EO/PO		4	4
Coconut fatty acid	0.5	0.7	0.7
MgSO4 7 H2O	0.9	0.75	0.75
Perfume (a)	0.7	0.7	0.7
Water	Balance	Balance	Balance
pH	std	Equal	
Grease cutting	std	Equal	
Neat			
Dilute		L	
Foam collapse (200 ppm)	std	Equal	
Residue	std	Equal	

Example 2

The following compositions in wt. % were prepared by simple mixing at 25°C:

	Ref.	Α	В	С	D	E	F
Sodium C ₁₃ -C ₁₇ paraffin	3.36	2	2	2	2	2	2
sulfonate	1		ļ		ļ		Į.
Levenol F-200	0.9					2	
LF300	0.9						2
Dobanol 91-5		2	2	2	2		
Diethylene glycol monobutyl ether	4.8						
Hexanol 5EO		4				4	4
Hexanol 4EO			4				
Hexanol 3EO				4			
Hexanol 2EO					4		
Coconut fatty acid	0.5	0.7	0.7	0.7	0.7	0.7	0.7
MgSO4 7 H2O	0.9	0.75	0.75	0.75	0.75	0.75	0.75
Perfume (a)	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Water	Balance						
Grease cutting Neat Dilute	std	Equal					
Foam collapse (200 ppm)	std	Equal					
Residue	std	Equal					

What Is Claimed:

- 1. A microemulsion cleaning composition comprising:
- (a) 0.1 wt. % to 8 wt. % of an anionic selected from the group consisting of sulfonated surfactants and sulfated surfactants;
- (b) 0.5% to 6% of a nonionic surfactant selected from the group consisting of an ethoxylated nonionic surfactant, an ethoxylated/propoxylated nonionic surfactant and a mixture of:

$$\begin{bmatrix} CH_2-\Theta-(CH_2CH-O-)_{\mathcal{K}}B \\ R' \\ CH-\Theta-(CH_2CH-O-)_{\mathcal{Y}}B \end{bmatrix}_{W}$$

$$\begin{bmatrix} CH_2-\Theta-(CH_2GH-O-)_{\mathcal{T}}B \\ CH_2-\Theta-(CH_2GH-O-)_{\mathcal{T}}B \\ \end{bmatrix}$$
(I)

and

5

10

15

20

$$\begin{array}{c} CH_{2} - O - (CH_{2}CH - O -)_{X} + I \\ \\ CH - O - (CH_{2}CH - O -)_{Y} + I \\ \\ CH_{2} - O - (CH_{2}CH - O -)_{Y} + I \end{array}$$

$$(II)$$

wherein w equals one, and B is selected from the group consisting of hydrogen and a group represented by:

25 wherein R is selected from the group consisting of alkyl group having 6 to 22 carbon atoms, and alkenyl groups having 6 to 22 carbon atoms, wherein at least one of the B groups is represented by said

R' is selected from the group consisting of hydrogen and methyl groups; x, y and z have a value between 0 and 60, provided that (x+y+z) equals 2 to 100, wherein in Formula (I) the weight ratio of monoester / diester / triester is 40 to 90 / 5 to 35 / 1 to 20, wherein the weight ratio of Formula (I) and Formula (II) is a value between 3 and 0.02:

- (c) 0.5% to 8% of a short chain amphiphiles formed from the condensation product of an alkanol, ethylene oxide and propylene oxide or an alkanol and ethylene oxide:
 - (d) 0.05% to 2% of a fatty acid:
 - (e) 0.25% to 6% of magnesium sulfate;
- (f) $$\rm 0.1\ to\ 5\ wt.\ \%}$ of a water insoluble hydrocarbon, essential oil or a perfume; and
 - (g) the balance being water.
- The cleaning composition of Claim 1 wherein the anionic surfactant is a
 C₁₃-C₁₇ paraffin sulfonate or a C₁₀-C₂₀ alkane sulfonate.
 - The cleaning composition of Claim 1, wherein the concentration of the water insoluble hydrocarbon, essential oil or perfume is 0.4 wt. % to 5 wt. %.
 - The cleaning composition of Claim 1 wherein said short chain amphiphile has the formula:

or

20

25

5

10

- wherein R_1 or R_2 are a straight or branched chain alkyl group having 2 to 6 carbon atoms and x or w is a number from 2 to 5 and y or z is a number from 1 to 4.
 - 5. The composition according to Claim 4, wherein R₁ has 6 carbon atoms.
 - The cleaning composition of Claim 1 wherein said short chain amphiphile has the formula:

R₁O—(CH₂CH₂O)_{II}——H

wherein R is a straight or branched chain alkyl group having 2 to 6 carbon atoms and n is a number from 2 to 8.

7. The composition according to Claim 6, wherein R₁ has 6 carbon atoms and n is a number from 3 to 6.